OFFICE OF NAVAL RESEARCH

Grant N00014-89-J-1178

R&T Code 413Q001-05

TECHNICAL REPORT No. #48

Pre-Oxidation Anneal Kinetics: Interface Degradation of Thin SIO_2 Films on Silicon

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MRS Proceedings 1992 Sp. Symposium "Chemical Surface Preparation, Passivation and Cleaning for Semiconductor Growth and Processing"

July 13, 1992

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	July 13, 1992	

4. TITLE AND SUBTITLE

Pre-Oxidation Anneal Kinetics: Interface Degradation Of Thin SIO_2 Films on Silicon

5. FUNDING NUMBERS

#N00014-89-J-1178

6. AUTHOR(S)

J.C. Poler and E.A. Irene

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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Chemistry Department
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

Technical Report #48

11. SUPPLEMENTARY NOTES

none

12a. DISTRIBUTION/AVAILABILITY STATEMENT

This document has been approved for public release and sale, distribution of this document is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS

thin films, degradation, tunneling currents

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	

MRS Proceedings 1992 Sp. Symposium "Chemical Surface Preparation, Passivation and Cleaning for Semiconductor Growth and Processing.

PRE-OXIDATION ANNEAL KINETICS: INTERFACE DEGRADATION OF THIN SiO_2 FILMS ON SILICON

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Abstract

The high temperature anneal of hydrogen terminated silicon has been shown to etch and roughen its surface. We attempt to describe the degree of this roughness and the time scale on which it occurs using several electrical measurements: excess direct tunneling currents, dielectric breakdown and the oscillations in the Fowler-Nordheim tunneling currents. From these results we draw conclusions on the time and water content dependence of pre-oxidation annealing on the microroughness of the Si/SiO_2 interface.

Introduction

The continued scaling down of design rules for ULSI technologies is focusing more attention on very thin, ~50Å, passivating films. Several adverse phenomena deemed negligible for thicker insulating films become critical for the thinner ones. It is known that microroughness at the Si/SiO_2 interface can seriously degrade the electrical characteristics of the insulating layer[1]. It has recently been shown[2] that surface preparation and pre-oxidation ambient conditions can alter the surface morphology of the silicon and the insulating integrity of the oxide in metal-oxide-semiconductor (MOS) capacitors.

Liehr[3] *et al* has shown that exposure of a hydrogen terminated silicon surface to a high temperature "inert" ambient can result in microroughening of the silicon. These phenomena have been explained in terms of the balancing of two competing reactions involving the silicon and low concentrations of oxygen[4] where:

$$Si + O_2 \rightarrow SiO_2(s) \qquad (1)$$

and

$$2Si + O_2 \rightarrow 2SiO(g) \qquad (2)$$

For a given partial pressure of the oxidizing species, there is a transition temperature above which the silicon etches, leaving a roughened surface. The insulating properties of a thin oxide grown on these surfaces is substandard, and results in low dielectric breakdown fields and large direct tunneling currents in the low field regime. In the present study, we report on the effects of a pre-oxidation anneal (PreOxA) in an "inert" ambient on the breakdown strengths and excess tunneling currents through thin oxides.

For some of the samples, where the interface was not too degraded, we were able to measure the I-V characteristics in the high field regime (>7MV/cm). At higher bias voltages (>4V) the currents are dominated by Fowler-Nordheim (FN) conduction:

$$I_{FN} = AV^2 \exp[-\frac{C}{V}] . \quad (3)$$

For films, where the inelastic mean free path of an electron, L_0, is on the same order as the thickness, the FN currents exhibit quantum oscillations in the I-V characteristic[5]. This is due to the interference of the coherent electrons in the "conduction" band of the insulating layer. The amplitude of the oscillations can be related to the abruptness of the film/anode interface. Microroughness of the appropriate dimensions will dampen these oscillations. We report on the effects that small concentrations of water during thermal processing have on the oscillations, and draw conclusions based on the microroughness model.

Experimental

A. Sample preparations: Single side polished, lightly and degenerately doped p-type Si(100) wafers were RCA cleaned, followed by a 10 second dip in concentrated hydrofluoric acid (HF). Some samples received a five minute treatment in a buffered hydrofluoric acid (BHF) solution of varying pH. This process left the wafer with a clean hydrogen terminated surface that is resistant to native oxide growth[6]. All solutions were MOS grade and the samples were rinsed in deionized water before film growth. Samples were blown dry in N_2 and loaded into the end cap of the furnace. Annealing and oxidations were carried out in a double walled fused silica horizontal tube furnace. High purity gasses were mixed into the furnace at a flow rate of ~4.7l/min. An effort was made to keep the tube sealed, with the gasses flowing through a hygrometer to avoid backstreaming of oxygen containing impurities. Dry oxidations were carried out with a H_2O concentration of less than 3 ppmV. All oxidations were carried out under ~1atm. pressure and 800°C. After film growth, the samples were quickly pulled, in O_2, to the end cap to cool in an inert ambient. Film thickness was determined by ellipsometry. Metal gates ~$8 \cdot 10^{-4}$ cm^2 in area, were deposited through a shadow mask by evaporating ~3000Å of aluminum at 25Å/s under a base pressure of $4 \cdot 10^{-7}$ torr. There was no post metal anneal (NPMA).

B. Pre-Oxidation Anneal: The samples that did not receive a PreOxA were placed in the end cap with O_2 flowing for 10 minutes to further drying, and warm up (~200°C). They were then pushed, in O_2, to the hot zone for oxidation. The PreOxA samples were also dried in the end cap but, an inert gas was flowing in the tube. The samples were quickly (<5sec.) pushed to the hot zone under a dry (<3ppmV H_2O) inert ambient of either Ar or N_2 at 800°C. The length of the anneal was varied, in no particular order, from ~0sec. to 45min. There is an offset in all of the anneal times due to the transition from inert to oxidizing gas. By measuring transients in H_2O concentrations as a function of time, and from gas flow rates we can estimate the length of this offset. It takes ~6sec. for the concentration of the oxidant to reach ~10% of its saturation value. The oxygen levels are near saturation in less that 60sec. The transition length should be constant for all anneals. For the runs labeled 0sec. PreOxA, the gasses were switched simultaneously with pushing the sample to the hot zone. All other anneal times were defined as the time from the sample push, until the ambient was switched

over to the oxidizer. There is also a thermal transition when the sample is first pushed to the hot zone. There is a ~68sec. rise time for the sample to reach 90% of its final temperature. This transient, although constant for all samples, adds some ambiguity to the interpretation of results for short pre-oxidation anneals.

C. Tunneling I-V Measurements: Contact was made to the gate with a tungsten probe. Back side contact to a pedestal was made by abrading the wafer and applying a GaIn eutectic paste. The voltage was applied to the substrate by driving a bipolar operational power supply amplifier with a linear voltage ramp. The currents were sensed at the gate with a logarithmic picoammeter. All measurements were automated and interfaced to a personal computer for acquisition and analysis. Several dots (8 - 10) on each wafer were probed and the results were averaged for analysis.

Results and Discussion

The dominant transport mechanisms are displayed in Fig. 1. At low bias (<1V), the small and constant displacement current I_d, from Gauss' law, is measured. I_d is subtracted from the I-V curve before analysis. At high bias, for a film of good quality, the current is dominated by Fowler-Nordheim (FN) type conduction. When the Fermi level of the gate is raised higher than the substrate/insulator work function potential, ϕ_{so}, electrons can tunnel through the triangular barrier (Fig. 2) into the insulators conduction band. This transport is described by Eqn. 3, where the tunneling distance is a function of the applied bias. When V_{gate} is below ϕ_{so} the electrons can tunnel directly from the gate to the substrate.

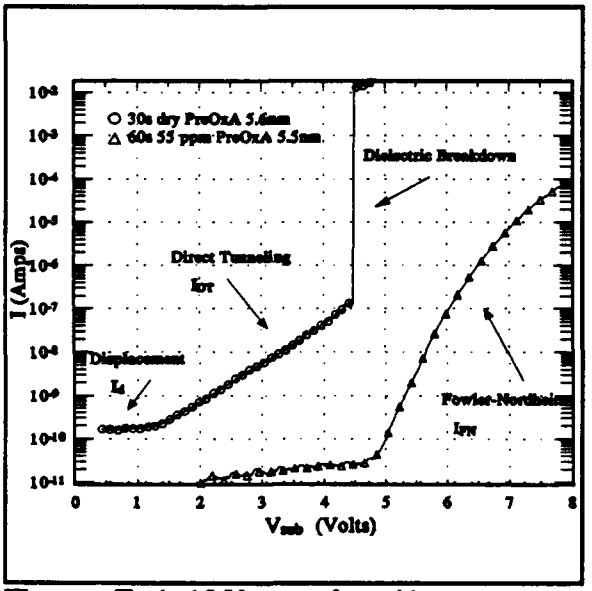

Figure 1. Typical I-V curves for oxides grown on p-Si(100) after a dry *(above)* and wet *(below)* PreOxA.

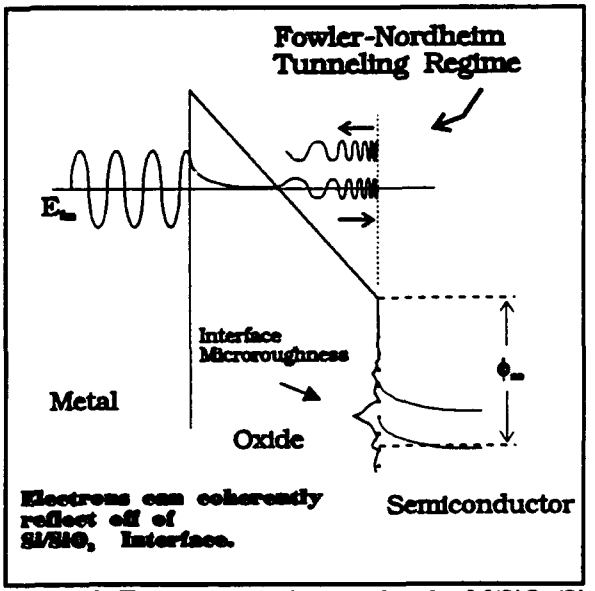

Figure 2. Energy band diagram for the $M/SiO_2/Si$ system. The quantum oscillation cavity and microroughness are illustrated.

This transport is governed by an exponential dependence on the potential across the structure:

$$I_{DT} = I_o \exp[G_T * V_{ox}] \quad (4)$$

where the direct tunneling current, I_{DT}, is a function of the oxide voltage, V_{ox}, and the constants G_T and I_o depend on the physical characteristics of the sample.

Using Eqn. 4, G_T can be obtained graphically and is interpreted as the differential conductivity of the structure. This conductivity varied between .8 and 1.1. I_o depends more on the dimensions of the structure. Variations in the area of the dots is partially removed by subtracting off the I_d. From the solution of the one electron Schroedinger equation, we learn that the tunneling current is exponentially dependent on the tunneling distance, d_{ox}. This dependence is represented in the direct tunneling current pre-exponential I_o. Since the injecting electrode area is large compared to the thickness of the film, the tunneling length is actually an effective distance d'_{ox} that averages over possible variations in thickness. Since the dependence is of an exponential form, the weighting for the average is strongly skewed toward the shortest distance. Perturbations in the film thickness, due to non-planar interfaces, will dominate the conduction mechanism.

Using I_o as a qualitative measure of interface roughness, we examined the effects that a pre-oxidation anneal had on the silicon surface. We grew several series of oxides, on both lightly and degeneratively doped p-Si(100). The pH of the final BHF dip was varied from ~1 to 9. A typical data set describing the dependance of I_o on the PreOxA time is shown in Fig. 3. From the fit of the data (solid line), and considering scatter in the data, it appears that I_o is independent of anneal time. Furthermore, substrate doping levels and pH variations did not have a significant effect on these results (data not shown).

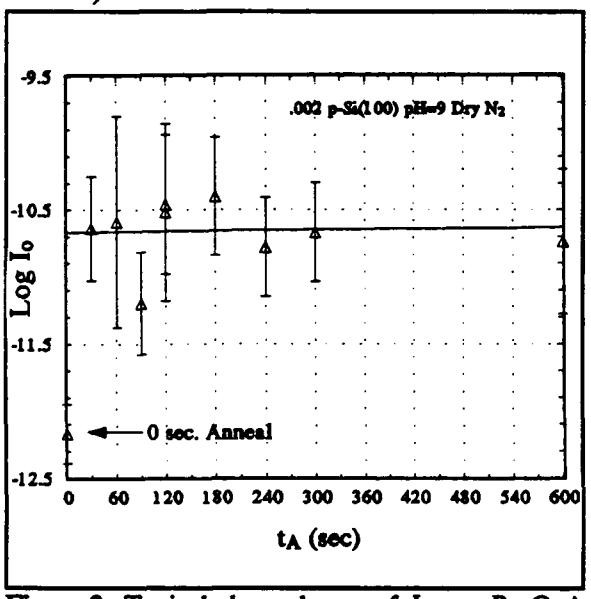

Figure 3. Typical dependance of I_o on PreOxA time. T_A=800°C <3ppmV H_2O.

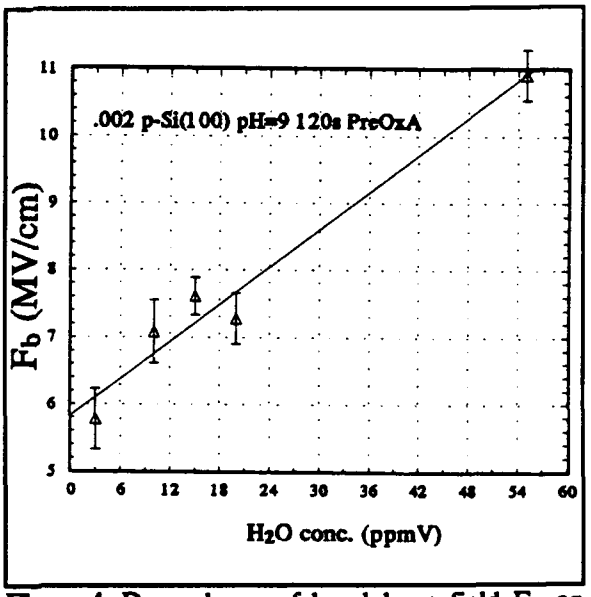

Figure 4. Dependance of breakdown field F_b on concentration of H_2O during Pre-oxidation anneal.

All of the samples that received a PreOxA in a dry (<3ppmV) ambient exhibited low dielectric breakdowns with the breakdown field, F_b, being independent of the length of the PreOxA and the sample preparation. Dielectric breakdown is known to be accelerated due to the damage incurred by injecting charge into the insulator. If the

anode interface contains microroughness resulting in protrusions on the surface there will be a localized increase in injected charge due to the field enhancement at these asperities. Therefore, the rougher the interface, the lower will be the apparent breakdown field.

The presence of small concentrations of H_2O in the gas during the PreOxA seems to temper the roughening mechanism. In Fig. 4, we see that there is a clear proportionality between the water concentration in the annealing gas, and the average breakdown field F_b. Because the water is also an oxidant, its presence drives the competition between reactions (1) and (2) toward the film growth mechanism. This decreases the overall etching rate. Apparently these surfaces do not get as damaged, perhaps the etching is more spatially uniform. It is also reported that the addition of H_2O during oxidation can reduce bulk oxide defects[7], yielding better breakdown statistics. However, in the present experiments, the H_2O is turned off as the oxidation starts. The measured H_2O concentrations drop quickly, and the majority of the oxide is grown under relatively dry conditions. Thus at this point we believe that this dependence is primarily a result of the surface morphology, and further evidence for this will be presented.

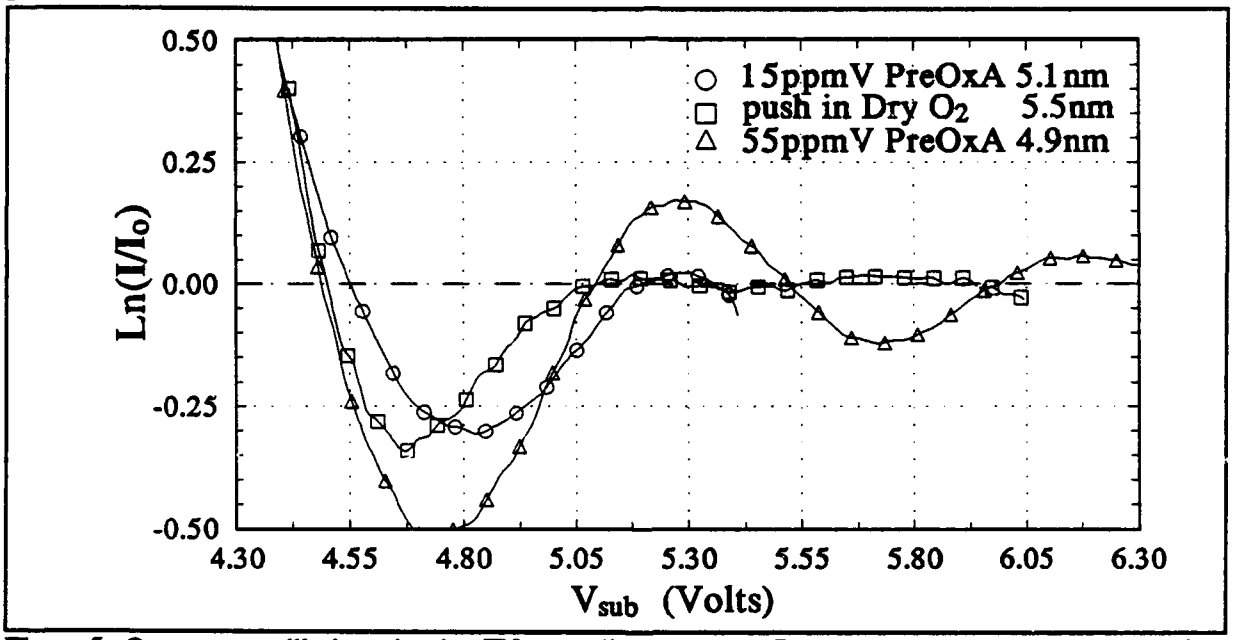

Figure 5. Quantum oscillations in the FN tunneling currents. Damped oscillations due to interface anomalies.

The oscillations in the FN tunneling currents due to the quantum interference of the electrons in the oxides conduction band, are sensitive to chemical and physical changes near the reflecting interface. It has been shown that these oscillations will be damped out due to thickness inhomogeneities in the film[8]. Inelastic phase randomizing collisions at the interface will also reduce the amplitude of the oscillations if the scale of the microroughness is on the order of the electrons wavelength. Scattering at the interface would simply decrease the amplitude, without shifting the positions of the extrema. Whereas, microroughness would contribute to an effective thickness different than that of a film with abrupt interfaces. This effective thickness would shift the

positions of the oscillations relative to a planar oxide. In Fig. 5, the effects on the oscillation amplitudes from adding H_2O to the anneal ambient are shown. It is seen that the largest oscillations correspond to the anneals with the highest H_2O concentrations. This result supports the microroughness argument, and correlates with the breakdown field observations. Although it is difficult to estimate the length scale, it would seem that these oscillations give a qualitative measure of the roughness at the silicon interface.

Summary

By using electrical methods, we examined the effect that a high temperature anneal in an inert gas had on the surface morphology of a clean silicon wafer. We concluded that this pre-oxidation anneal degraded the Si/SiO_2 interface. This degradation appeared to result in microroughness at the interface. This was manifest in the enhanced direct tunneling currents, lower dielectric breakdown fields and the damping of quantum oscillations in the FN tunneling currents. This degradation took place on a short time scale and seemed to reach a steady state, independent of anneal time. The addition of small concentrations of H_2O during the anneal decreased these effects and resulted in a superior electrical character for the MOS structures.

Acknowledgements

This work was supported in part by the Office of Naval Research (ONR), and through a fellowship to one of us (JCP) by the Semiconductor Research Corporation (SRC) Competitiveness Foundation. We are grateful to Drs. D.J. DiMaria and M.V. Fischetti for helpful discussions about FN quantum oscillations.

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